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Molecular structures of di-benzylidene cyclohexanone

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The cell constants for the complex $C_{20}H_{18}O$ are $a = 10.40 \pm .01$Å, $b = 18.24 \pm .01$Å, $c = 9.50 \pm .01$Å, $\alpha = \gamma = 90°$, $\beta = 121.74° \pm 0.1°$. There are four molecules in each unit cell. The crystal belongs to the space group $P2_1/n$. Patterson synthesis projected along the three axes show that the planes of all the three rings of the molecule are either parallel or make an angle of about 90° to each other. Also, the molecular formula should be 2,5-bis (benzylidene)-cyclohexanone. The molecule lies along the longest b-axis with little inclination to b-axis.

1. INTRODUCTION

This paper deals with the detailed analysis for cell constants and Patterson map. The crystals of di-benzylidene cyclohexanone are well developed and yellow in colour (Weast 1968-69). The crystals were studied under microscope and found hexagonal in shape on b-face (figure 2).

The crystal of di-benzylidene cyclohexanone $C_{20}H_{18}O$ contains three hexagonal closed rings connected by C-atoms as shown in figure 1 (Rakoff & Rose 1966).

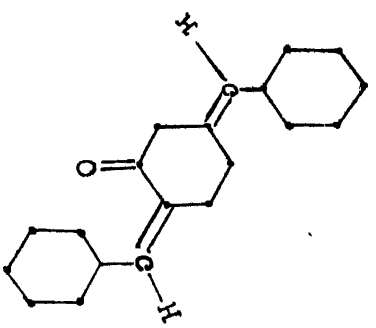

Fig. 1

The benzylidene groups may be attached to 2,5 or 2,4 positions of cyclohexanone. The carbons which interlink the rings from trigonal bonding. The

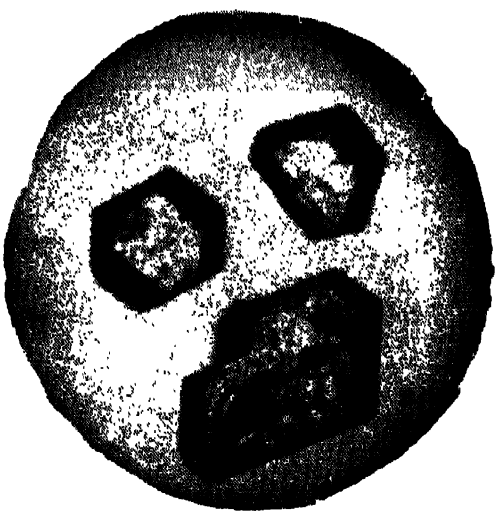

Fig. 2.

two benzylidene groups may rotate with respect to the cyclohexanone group and may make angle with the plane of cyclohexanone. The purpose of the present study is to investigate the 2,5 or 2,4 arrangements, relative orientation of the closed rings and positions of the molecule in unit cell.

2. Experimental

2.1. *Measurement of the cell constants*

The oscillation photographs about a, b and c-axis were taken using CuK_α radiation by a camera of diameter 5.73 cm. The axial lengths were obtained from these oscillation photographs and finally obtained from Al-calibrated zero layer Weissenberg photographs about all the three axes with 2° rotation of the crystal per 1 mm. translation of the camera. The values thus obtained are given below :

$$a = 10.4+0.01\text{Å}, \qquad b = 18.24+0.01\text{Å}, \qquad c = 9.50+0.01\text{Å},$$
$$\alpha = \gamma = 90°, \qquad \beta = 121.74+0.1°.$$

2.2. *Determination of the density of the crystal* :

The density of the crystal has been determined by the method of flotation using a mixture of $Zn\,Br_2$ ($\rho = 1.70$ gm/cc) and xylene ($\rho = 1.06$ gm/cc). The density of the crystal comes out to be 1.20 gm/cc. Assuming four molecues in unit cell the density of the crystal has been calculated and found to be 1.19 gm/cc.

2.3. *Determination of the space group of the crystal*

There is no systematic absences for *hkl* reflexions indicating the cell to be primitive. The intensities of the zero layer oscillation photographs on equatorial line only about the b-axis shows that the crystal is monoclinic. The intensities on the Weissenberg photographs also show that

$$|F_{hkl}|^2 = |F_{\bar{h}kl}|^2 \neq |F_{\bar{h}kl}|^2 \quad \text{and} \quad |F_{\bar{h}kl}|^2 = |F_{hkl}|^2$$

which indicates that the crystal is monoclinic. For *oko* reflections $k = 2n$ condition showed the presence of two fold screw axis 2_1. The classifications of the reflections are as follows :

Class of reflections	*Present for*
hkl	No condition
oko	$k = 2n$
hol	$h+1 = 2n$

The study of the above systematic absences suggests uniquely that the crystal belongs to the space group $P2_1/n$.

2.4. *Measurement of intensities and their corrections* :

Zero layer Weissenberg photographs along all the axes using Robertson-multiple-film technique (5 films) were recorded on a Nonius Weissenberg camera using CuK_α radiation. The corresponding intensities for different reflections were computed with the help of intensity scale calibrated before. These intensities were then corrected for Lorentz and polarization factors using L.P. correction programme (3.4) on IBM-1620. The linear absorption coefficient of the compound has been calculated ($\mu = 5.67$ cm^{-1}). The absorption errors seem to be negligible.

2.5. *Sharpend Patterson Synthesis*

The space group $P2_1/n$ has three patterson projections Pmm, $P2$ and Pmm about a, b and c-axis respectively. For the plane group Pmm about a axis, the Patterson function

$$P(yz) = \frac{1}{A_0}\left[|F_{oo}|^2 + 2\{\sum_1^\alpha l\,|F_{ol}|^2 \cos 2\pi lz + \sum_1^\alpha K\,|F_{ok}|^2 \cos 2\pi Ky\}\right.$$

$$\left. + 4\sum_1^\alpha\sum_1^\alpha K\,|F_{kl}|^2 \cos 2\pi lz.\cos 2\pi Ky\right].$$

For the plane group $P2$ about b-axis, the Patterson function

$$P(xy) = \frac{1}{A_0}\left[|F_{oo}|^2 + 2\sum_1^\alpha h\,|F_{ho}|^2 \cos 2\pi hx + 2\sum_1^\alpha l\,|F_{ol}|^2 \cos 2\pi lz + 2\sum_1^\alpha h\sum_1^\alpha l\right.$$

$$\left.\times\{|F_{hl}|^2 \cos 2\pi(hx+lz) + |F_{\bar{h}l}|^2 \cos 2\pi(-hx+lz)\}\right].$$

For c-axis projection the Patterson function $P(xy)$ can be obtained from above expression for $P(yz)$ replacing z by x and l by h.

Now if we consider the atoms as point atoms then ${}^s f_{hkl} = F_{hkl}/\hat{f}_{hkl}$ where F_{hkl} is called sharpened $F = {}^sF_{hkl}$ considering atoms as point atoms. $\hat{f}_{hkl}$ = average atomic scattering factor scaled to unit scattering power which is equal to f/Z. The sharp $|{}^sF|^2$ have been used instead of normal $|F|^2$ to draw sharpened patterson maps about a, b and c-axis. These maps have been shown in figures 2, 3 and 4 respectively.

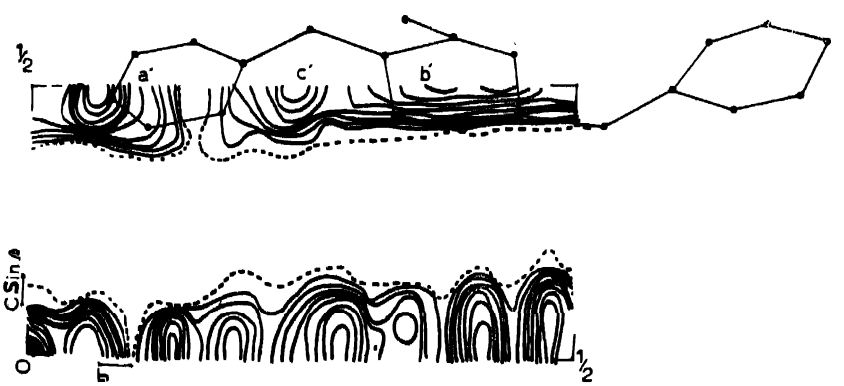

Fig. 3

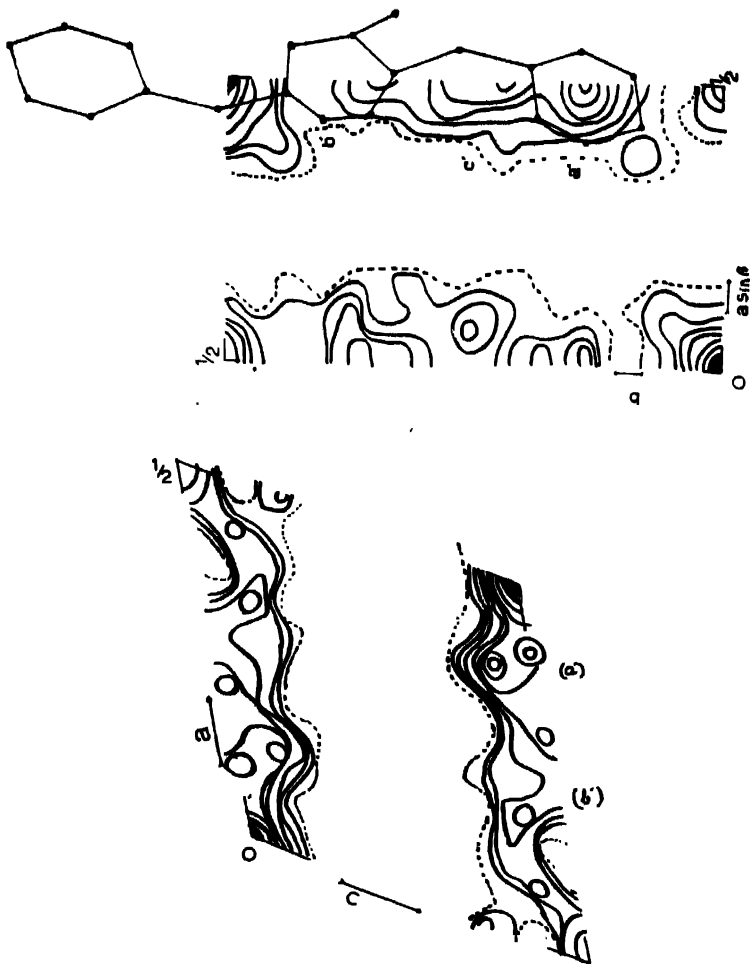

Fig. 4

2.6. *Symmetric Vectors*

There are four equivalent positions with co-ordinates x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; and the symmetric vectors are $2x, 2y, zz$; $\frac{1}{2}$, $\frac{1}{2}-2y$, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}+2y$, $\frac{1}{2}$; $\frac{1}{2}+2x$, $\frac{1}{2}$, $\frac{1}{2}+2z$; $2x$, $-2y$, zz; $\frac{1}{2}-2x$, $\frac{1}{2}$, $\frac{1}{2}+zz$.

2.7. *Interpretation of Patterson Map*

On Patterson maps along a and c-axis, three major peaks designated by (a'), (b'), (c') lie on Harkerline at $V = \frac{1}{2}$. Three rings can be accommodated on these peaks making an angle 45° with the plane of projections. Thus the plane of each ring may be parallel or makes angle of 90° with each other because these peaks lie on the mirror. A model of the molecule with the dibenzylidene at 2,5 position of cyclohexanone has been projected along a and c-axis, while all the

rints are mutually parallel as shown in the patterson maps. Also it can be seen that the molecule lies along the longest b-axis.

On b-axis patterson maps two peaks namely (a'), (b') are available. The (b') peak appears due to image of the molecule around the origin. Therefore all the rings, may be accommodated in a-axis map in consistence with the other two maps. These show that the molecules lie more or less along y-axis.

In view of the facts that the molecule is large and there is severe overlapping of the peaks in the patterson projections. No attempt has been made to continue the work in determining the co-ordinates of all the atoms.

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